

CHEMICAL EXAMINATION  
OF THE ROOT OF  
IPOMOEA ORIZABENSIS

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## I.—*Chemical Examination of the Root of Ipomoea orizabensis.*

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THE root of *Ipomoea orizabensis*, Ledanois (Nat Ord. *Convolvulaceae*) has attracted considerable attention in recent years on account of having been brought into commerce under the name of "Mexican Scammony Root," and the fact that the resin prepared therefrom has displaced to a considerable extent the true scammony resin (from *Convolvulus Scammonia*, Linné), the two products having been generally considered to be chemically identical.

The root under consideration has been described in the "Pharmacographia," 2nd edit., p. 446, and more recently by Mr. E. M. Holmes (*Pharm. J.*, 1904, **72**, 326). It is known under various names besides that above mentioned, such as "Light, Fusiform, or Woody Jalap," "Orizaba Root," and to the Mexicans as *Purgo macho*.

The resin obtained from the above-mentioned root, which is usually stated to be completely, or almost completely, soluble in ether, has been the subject of several more or less extended investigations (compare van Ryn, "Die Glykoside," p. 396, and Tschirch, "Die Harze," Bd. II., p. 886). Among the earliest of these investigations may be mentioned those of Johnston (*Phil. Trans.*, 1840, Part II., p. 342), Kayser (*Annalen*, 1844, **51**, 101), and Mayer

(*Annalen*, 1855, **95**, 129), the last-mentioned author having given to the resin from *Ipomoea orizabensis* the name "jalapin"\* ("jalappin"), whilst the resin of jalap, or the portion of the latter insoluble in ether, was designated "convolvulin." To the so-called "jalapin," the glucosidic character of which was recognised, Mayer assigned the formula  $C_{34}H_{56}O_{16}$ . He stated that by the action of alkalis it is converted into "jalapic acid,"  $C_{34}H_{60}O_{18}$ , a yellow, amorphous mass, which is readily soluble in water or alcohol, and that on heating either jalapin or jalapic acid with dilute acids they are resolved into sugar and "jalapinol" or "jalapinolic acid," the latter having been given the formula  $C_{16}H_{30}O_3$ .

Spirgatis (*Annalen*, 1860, **116**, 289), as also Poleck (*Chem. Centr.*, 1892, II., p. 786), believed to have proved the identity of jalapin with the resin of scammony or "scammonin," and this was subsequently affirmed by Kromer (*Chem. Centr.*, 1895, II., pp. 228, 449, 495). The last-mentioned investigator, who has most recently assigned to jalapin the formula  $C_{49}H_{90}O_{23}$ , or



(*Arch. Pharm.*, 1901, **239**, 388), showed that by the action of alkalis on the convolvulaceous resins, not only the respective "glucoside acids" are produced, but also volatile acids, as well as acidic substances which are soluble in ether and not volatile in steam; thus the jalapin from *Ipomoea orizabensis*, on treatment with barium hydroxide, was stated (*loc. cit.*, p. 373) to yield, besides the so-called jalapic acid,  $\alpha$ -methylbutyric and tiglic acids, together with a tetrahydroxydecylic acid,  $C_{10}H_{20}O_6$ .

The previously-mentioned jalapinolic acid, which crystallises in small, colourless needles, was made the subject of a special investigation by Kromer (*J. pr. Chem.*, 1898, [ii], **57**, 448). He found it to melt at 67—68°, and to possess the formula  $C_{16}H_{32}O_3$ , also stating it to be optically inactive. Several derivatives of the acid were prepared, and, having thus ascertained that it was not identical with  $\alpha$ -hydroxypalmitic acid, it was considered, in view of its chemical behaviour, to be represented by the formula



Notwithstanding the number of investigations relating to the so-called "jalapin," as indicated by the brief survey of the literature given above, it has appeared to us that a more complete examination of this product was desirable, especially as the statements concerning its composition and chemical characters are so confused

\* The term "jalapin" was originally applied to the chief portion of jalap resin, which is insoluble in ether, and it appears still to retain this meaning in England, but in order to avoid further confusion the name is employed in this communication in the sense denoted by Mayer.



and divergent. With consideration of the facts already known, it is obvious that the resin in question cannot be regarded as a definite compound, or represented by any one of the numerous formulæ hitherto assigned to it. As the present authors have recently shown (*J. Amer. Chem. Soc.*, 1910, **32**, 80) that the true jalap resin (from *Ipomoea Purga*, Hayne), commonly designated "convolvulin," does not consist of a single definite glucoside, but is an exceedingly complex mixture, the constituents of which are not entirely glucosidic, it was thought probable that the same conditions would exist with regard to other convolvulaceous resins, and the correctness of this conclusion has now been rendered evident.

Although the primary object of the present investigation of "Mexican Scammony Root" was to determine more exactly the chemical characters of the resin prepared therefrom, consideration has also been taken of its other constituents.

#### EXPERIMENTAL.

The material employed for this investigation consisted of a bale of the so-called "Mexican Scammony Root," which conformed in its characters to the recorded description (*loc. cit.*) of the root of *Ipomoea orizabensis*, Ledanois, and its authenticity was kindly confirmed by Mr. E. M. Holmes, F.L.S.

As a preliminary experiment, 50 grams of the ground material were successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 40—60°)	extracted	0.55 gram.	=	1.10 per cent.
Ether	,,	4.92	,,	9.84
Chloroform	,,	0.48	,,	0.96
Alcohol	,,	5.09	,,	10.18

Total 11.04 grams = 22.08 per cent.

*Determination of the Total Resin.*—Fifty grams of the ground root were completely extracted with hot alcohol in a Soxhlet apparatus. To the liquid thus obtained, 25 c.c. of water were added, the alcohol then evaporated, and the separated resin thoroughly washed with hot water, after which it was dried in a water-oven until of constant weight. The mean of two nearly concordant determinations was an amount equivalent to 14.55 per cent. of resin in the root. The proportion of this crude resin which was soluble in ether, as determined by its complete extraction in a Soxhlet apparatus, was equivalent to 71 per cent. of its weight.

*Extraction of the Root with Alcohol.*

For the purpose of a complete examination of the constituents of the root, a quantity (48·76 kilograms) of the ground material was extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, 15·59 kilograms of a soft, dark-coloured extract were obtained.

*Isolation of Sucrose.*

Inasmuch as it has been shown by Requier (*J. Pharm. Chim.*, 1905, [vi], **22**, 435, 492) that scammony root contains sucrose as well as reducing sugar, it was deemed desirable to ascertain whether sucrose is also contained in the root of *Ipomoea orizabensis*. For this purpose about 1 kilogram of the above-mentioned alcoholic extract was mixed with water to separate the resin, the dark-coloured aqueous liquid filtered, and treated with an excess of milk of lime. The mixture was then filtered, the alkaline filtrate saturated with carbon dioxide, again filtered, and the clear liquid evaporated under diminished pressure to the consistency of a syrup. By treating the latter with successive portions of alcohol, a product was finally obtained, which was completely soluble in 85—90 per cent. alcohol, and, after inoculation with a trace of sucrose and keeping for a few days, deposited a small amount (0·3 gram) of a substance in colourless prisms. After recrystallisation from slightly diluted alcohol, the substance melted at 184—185°, as did also a specimen of pure sucrose when heated somewhat rapidly, although the melting point of the latter is usually stated to be 160°. The general properties and an analysis of the substance definitely established its identity as sucrose. (Found, C=42·1; H=6·8. Calc., C=42·1; H=6·4 per cent.)

*Distillation of the Extract with Steam. Separation of an Essential Oil.*

A quantity (2 kilograms) of the above-mentioned extract was mixed with water, and distilled in a current of steam. The distillate, which contained some oily drops floating on the surface, was extracted with ether, the ethereal liquid being dried and the solvent removed, when a small amount (0·9 gram) of a pale yellow essential oil was obtained. This possessed a persistent odour, and gave the colour reaction for furfuraldehyde.

After the above-described operation, there remained in the distillation flask a dark-coloured aqueous liquid (A) and a quantity of a soft resin (B). The resin was repeatedly washed with hot water



until the latter remained colourless, and the washings added to the main portion of the aqueous liquid.

*Examination of the Aqueous Liquid (A).*

*Isolation of Scopoletin,  $(\text{CH}_3\cdot\text{O})(\text{OH})\text{C}_6\text{H}_2\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{O}$ .*

The aqueous liquid was concentrated under diminished pressure to the volume of about 5 litres, and repeatedly extracted with ether. The ethereal liquid was then shaken successively with aqueous ammonium carbonate and sodium carbonate, and finally with a 10 per cent. solution of sodium hydroxide. Only a small amount of a fluorescent substance was removed by this treatment, and on subsequently drying and evaporating the ethereal liquid nothing remained. The original aqueous liquid was then extracted repeatedly with chloroform, and the chloroform extracts shaken with aqueous sodium carbonate, when a further quantity of the fluorescent substance was removed. The sodium carbonate extracts from both the ethereal and chloroformic liquids were united, acidified, and shaken with chloroform, when, after drying and evaporating the solvent, a quantity (0.9 gram) of a crystalline substance was obtained. On recrystallisation from absolute alcohol, it separated in pale yellow needles, which melted at 203—204°, and gave with alkalis a brilliant, blue fluorescence. (Found, C=62.6; H=4.3. Calc., C=62.5; H=4.2 per cent.)

An acetyl derivative, prepared by heating the substance with acetic anhydride, separated from absolute alcohol in slender, colourless needles, melting at 177°. The substance was thus identified as scopoletin (4-hydroxy-5-methoxycoumarin), which has previously been obtained from several plants (compare Trans., 1911, **99**, 1043).

The original aqueous liquid, which had been extracted with both ether and chloroform as above described, was next shaken with successive portions of amyl alcohol, these amyl alcoholic liquids being then united, washed with water, and concentrated under diminished pressure. A dark-coloured, syrupy product was thus obtained, which was almost insoluble in cold, but completely soluble in hot, water.

*Isolation of 3:4-Dihydroxycinnamic Acid,*  
 $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ .

The above-mentioned syrupy product was heated for a few minutes with a 10 per cent. solution of potassium hydroxide, the liquid then cooled, acidified, and extracted with ether. The

ethereal liquid was afterwards shaken with four successive portions of aqueous ammonium carbonate, and the alkaline liquids separately acidified, when crystalline precipitates were produced. On subsequently extracting the ethereal liquid with solutions of sodium carbonate and sodium hydroxide, only amorphous products were obtained, and on finally evaporating the ether, nothing remained. The above-mentioned crystalline precipitates were found to be identical, and the whole was therefore recrystallised from hot water containing a little alcohol. The substance was thus obtained in pale yellow, prismatic needles, which melted and decomposed at  $223\text{--}225^\circ$  with evolution of gas, and this melting point was not changed by further crystallisation. The total amount of substance was 12 grams. In aqueous solution it gave a dark green colour with ferric chloride. After drying at  $110^\circ$ , it was analysed. (Found,  $\text{C}=60\cdot2$ ;  $\text{H}=4\cdot7$ . Calc.,  $\text{C}=60\cdot0$ ;  $\text{H}=4\cdot4$  per cent.)

The substance thus appeared to be 3:4-dihydroxycinnamic acid (caffeic acid), the melting point of which, however, has been variously recorded as  $185^\circ$ ,  $209^\circ$ , and  $213^\circ$ .

In order further to confirm the identity of the acid, a portion of it was methylated by means of methyl sulphate, and the product recrystallised from absolute alcohol. It separated in needles melting at  $180\text{--}181^\circ$ , and this melting point was not altered when mixed with pure 3:4-dimethoxycinnamic acid (Trans., 1910, **97**, 1946).

Another portion of the acid was acetylated by boiling with acetic anhydride. On crystallising the product from dilute alcohol, the diacetyl derivative separated in needles melting at  $198^\circ$ , the melting point of this compound having previously been recorded as  $190\text{--}191^\circ$  (Ber., 1878, **11**, 657).

*Methyl 3:4-Dihydroxycinnamate*,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\cdot\text{CH}_3$ .—As this compound appears not to have previously been prepared, a small quantity of the respective acid was dissolved in methyl alcohol, and the solution saturated with dry hydrogen chloride. The product of the reaction was poured into water, and the mixture extracted with ether, the ethereal liquid being washed with water and aqueous sodium carbonate, dried, and the solvent removed. A substance was thus obtained, which, when recrystallised from dilute alcohol, separated in pale yellow needles, melting at  $158\text{--}160^\circ$ :

0.1744 gave  $0\cdot3962\text{ CO}_2$  and  $0\cdot0846\text{ H}_2\text{O}$ .  $\text{C}=61\cdot9$ ;  $\text{H}=5\cdot4$ .

$\text{C}_{10}\text{H}_{10}\text{O}_4$  requires  $\text{C}=61\cdot8$ ;  $\text{H}=5\cdot2$  per cent.

The original aqueous liquid, which had been extracted with amyl alcohol as above described, was heated in a current of steam in order to expel the last traces of the alcohol, and to the warm liquid a slight excess of a solution of basic lead acetate was added, when



a copious, yellow precipitate was produced. This precipitate was collected, washed, and then suspended in water, and decomposed by hydrogen sulphide. On filtering the mixture, and concentrating the filtrate, a dark brown liquid was obtained, which gave a green colour with ferric chloride, but did not precipitate gelatin. After treating the liquid with a solution of potassium hydroxide, as previously described, a further small quantity of 3:4-dihydroxycinnamic acid was obtained.

The filtrate from the precipitate produced by basic lead acetate was treated with hydrogen sulphide for the removal of the excess of lead, the mixture again filtered, and the filtrate concentrated under diminished pressure to the consistency of a syrup, which, on cooling, formed a viscid jelly. The syrup instantly reduced Fehling's solution on heating, and yielded *d*-phenylglucosazone, melting at 205—206°. In order further to confirm the identity of the sugar, a portion of the syrup was heated with acetic anhydride in the presence of a little *d*-camphorsulphonic acid. A crystalline acetyl derivative was thus obtained, which melted at 130—131°, and was identified as  $\beta$ -penta-acetyldextrose. Inasmuch as the original alcoholic extract has been shown to contain a small amount of sucrose, which would doubtless have become inverted during the subsequent operations of heating, it is probable that the above-mentioned syrup, in addition to dextrose, also contained some lævulose. There was, however, no evidence of the presence of a methylpentose.

A portion (50 grams) of the above-mentioned syrup was heated with 5 per cent. sulphuric acid, and the liquid extracted with chloroform, when a very small amount (0.1 gram) of scopoletin was obtained, thus indicating the presence of a glucoside of this substance. The attempts which were made to isolate a glucoside from the syrup were, however, unsuccessful.

#### *Examination of the Resin (B).*

The crude resin, which had been separated from the aqueous liquid (A) as previously described, formed a dark brown mass, which, when dry, could be reduced to a light brown powder, and when treated with a little animal charcoal was obtained nearly colourless. After drying in a vacuum over sulphuric acid, it melted at 125—130°.

#### *Optical Rotation of the Crude Resin.*

Since the optical rotatory power of the various convolvulaceous resins has been considered to be a factor of some value in deter-

mining their identity and purity (compare Guigues, *Chem. Zentr.*, 1907, I., p. 309; also Power and Rogerson, *Amer. J. Pharm.*, 1908, **80**, 251, and *J. Amer. Chem. Soc.*, 1910, **32**, 85), it was deemed of interest to ascertain the optical rotation of the resin under investigation. For this purpose a portion of the resin obtained by the previously mentioned assay of the root was first employed. It was dissolved in absolute alcohol, and the solution heated with successive small portions of animal charcoal until nearly deprived of colour. The initial rotation of this solution in a 1-dcm. tube was  $-1^{\circ}51'$ , and since the amount of resin in 5 c.c. of the liquid was 0.4022 gram, therefore  $[\alpha]_D = -23.0^{\circ}$ . Another determination was made, with the use of a little of the above-described resin (B), which gave the following result:

A solution in absolute alcohol, of which 5 c.c. contained 0.2386 gram of resin, gave  $[\alpha]_D -1^{\circ}6'$  in a 1-dcm. tube, whence  $[\alpha]_D -23.05^{\circ}$ .

Guigues (*loc. cit.*) considers the specific rotation of the resin from *Ipomoea orizabensis* to be within the limits of  $-23.5^{\circ}$  and  $-25^{\circ}$ , and Kromer (*Chem. Centr.*, 1895, II., p. 228) has observed for purified "jalapin" the values  $-22.84^{\circ}$  to  $-23.83^{\circ}$ . The resin of scammony root, which, as previously noted, has been considered to be identical with "jalapin" (from *Ipomoea orizabensis*), has been stated by Guigues (*Bull. Soc. chim.*, 1908, [iv], **3**, 872) to have an optical rotation varying from  $-18.5^{\circ}$  to  $-23.5^{\circ}$  (Kromer, *loc. cit.*, states  $-23.06^{\circ}$ ), whilst the resin extracted from the gum-resin scammony has a maximum value of  $-24.5^{\circ}$ . Goris and Fluteaux (*Bull. Sci. Pharmacol.*, 1910, **17**, 15) have observed for the last-mentioned product a specific rotation of  $-24^{\circ}26'$ .

#### *Preliminary Extraction of the Crude Resin with Different Solvents.*

In order to ascertain the general characters of the crude resin, a small portion (10 grams) of it was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with various solvents. The amounts of extract, dried at  $100^{\circ}$ , were as follows:

Petroleum (b. p. $40-60^{\circ}$ ) extracted	6.2 per cent.
Ether	64.8 "
Chloroform	0.6 "
Ethyl acetate	24.8 "
Alcohol	2.3 "
Loss	1.3 "
<hr/>	
100.0 per cent.	

For the purpose of a complete examination, 1142 grams of the resin were employed. This was dissolved in alcohol, mixed with



purified sawdust, and the thoroughly dried mixture then successively extracted in a large Soxhlet apparatus with the above-mentioned solvents.

### I.—*Petroleum Extract of the Resin.*

This extract, after the removal of the solvent, was a dark brown, soft solid, amounting to 71 grams. It was dissolved in ether, and the ethereal solution extracted successively with aqueous ammonium carbonate and potassium carbonate, which, however, removed nothing. A subsequent extraction with a solution of sodium hydroxide removed only a very small amount of fatty material, which could not be obtained crystalline, and a trace of a yellow substance which gave a bright red colour with both acids and alkalis. The ethereal liquid was then washed with a little water, dried, and the solvent removed, when a quantity of a soft solid remained. This was dissolved in alcohol, and heated for about four hours in a reflux apparatus with an excess of potassium hydroxide, after which the mixture was diluted with water, and the alcohol removed in a current of steam. The alkaline liquid was then thoroughly extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when a crystalline residue was obtained.

#### *Isolation of Hentriacontane, $C_{31}H_{64}$ , and a Phytosterol, $C_{27}H_{46}O$ .*

The above-mentioned crystalline residue was dissolved in warm alcohol, when, on cooling, a small amount of a solid was deposited, which was collected and recrystallised from ethyl acetate. Two fractions were thus obtained, the first being very small in amount and melting at  $60-62^{\circ}$ , whilst the second fraction separated in plates, melting at  $133-135^{\circ}$ . The first fraction gave the colour reaction of the phytosterols, and it was therefore heated for a short time with a little phthalic anhydride. After this treatment there was isolated from the mixture a small amount of a hydrocarbon, which separated from ethyl acetate in leaflets melting at  $66-68^{\circ}$ . This substance was evidently hentriacontane,  $C_{31}H_{64}$  (m. p.  $68^{\circ}$ ), and when mixed with a little of this hydrocarbon of known purity the melting point remained unchanged.

The alcoholic liquid from which the above-mentioned solid had separated was concentrated, when a further quantity (1.1 grams) of substance was deposited in the form of leaflets. This was mixed with the previously obtained fraction (0.2 gram) melting at  $133-135^{\circ}$ , and the whole recrystallised from a mixture of ethyl

acetate and dilute alcohol. The substance was thus obtained in handsome, pearly leaflets, melting at 135—136°, and it gave the colour reaction of the phytosterols:

0.3192, on heating at 110°, lost 0.0153 H<sub>2</sub>O. H<sub>2</sub>O=4.8.

0.1072 \* gave 0.3292 CO<sub>2</sub> and 0.1144 H<sub>2</sub>O. C=83.7; H=11.8.

C<sub>27</sub>H<sub>46</sub>O, H<sub>2</sub>O requires H<sub>2</sub>O=4.5 per cent.

C<sub>27</sub>H<sub>46</sub>O requires C=83.9; H=11.9 per cent.

A determination of the specific rotatory power gave the following result:

0.1934,\* made up to 20 c.c. with chloroform, gave  $\alpha_D -0.39'$  in a 2-dcm. tube, whence  $[\alpha]_D -33.6^\circ$ .

The acetyl derivative was prepared by heating a little of the substance with acetic anhydride. It separated in flat needles, melting at 122—124°.

The above-described substance was thus definitely identified as a phytosterol, and, with the exception of the slightly higher melting point of its acetate, it agrees in character with verosterol (Trans., 1910, **97**, 1951).

#### *Isolation of Cetyl Alcohol, C<sub>16</sub>H<sub>34</sub>O.*

The alcoholic mother liquors remaining from the separation of the above-described phytosterol were evaporated, and the residue distilled under diminished pressure. The distillate was collected in three fractions, which passed over respectively at 190—200°, 200—220°, and 220—300°/15 mm. The first two fractions were united and recrystallised, first from light petroleum and then from ethyl acetate. A quantity (2.5 grams) of cetyl alcohol was thus obtained, which separated in small, colourless leaflets, melting at 50—51°. (Found, C=79.0; H=14.0. Calc., C=79.3; H=14.1 per cent.)

The third of the above-mentioned fractions, which was very small in amount, was crystallised from ethyl acetate, when it separated in laminæ, melting at 55—56°. It apparently consisted of a mixture of cetyl alcohol and some higher alcohol of that series.

The alkaline liquid, from which the above-described products had been removed by extraction with ether, was acidified, and again extracted with ether. The ethereal liquid was first shaken with aqueous ammonium carbonate, which removed a small amount (1.0 gram) of the previously-described 3:4-dihydroxycinnamic acid (m. p. 222—225°). It was next extracted with a solution of sodium carbonate, which removed all of the dissolved substance. The

\* Anhydrous substance.



alkaline liquid thus obtained was acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent evaporated, when a quantity of fatty acids remained.

### *Identification of the Fatty Acids.*

The above-mentioned mixture of fatty acids was distilled under diminished pressure, when it passed over between  $220^{\circ}$  and  $255^{\circ}/15$  mm. as a light, yellow oil, and amounted to 18 grams. The acids were first separated into liquid and solid portions by means of their lead salts.

*The Liquid Acids.*—These acids, when distilled under diminished pressure, passed over between  $220^{\circ}$  and  $235^{\circ}/15$  mm. as a pale yellow oil, and amounted to 9.2 grams. An analysis and a determination of the iodine value gave the following results:

0.1830 gave 0.5160  $\text{CO}_2$  and 0.1862  $\text{H}_2\text{O}$ .  $\text{C}=76.9$ ;  $\text{H}=11.3$ .

0.5154 absorbed 0.8226 iodine. Iodine value=159.6.

$\text{C}_{18}\text{H}_{34}\text{O}_2$  requires  $\text{C}=76.6$ ;  $\text{H}=12.1$  per cent. Iodine value=90.1.

$\text{C}_{18}\text{H}_{32}\text{O}_2$  „  $\text{C}=77.1$ ;  $\text{H}=11.4$  „ „ Iodine value=181.4.

From these results it would appear that the liquid acids consisted chiefly of linolic acid, with a relatively small proportion of oleic acid. This was further confirmed by the oxidation of a portion (8 grams) of the mixture with potassium permanganate, according to the method described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, I., p. 360). The chief product of the oxidation was tetrahydroxystearic acid, melting at  $158\text{--}160^{\circ}$ . (Found,  $\text{C}=61.9$ ;  $\text{H}=10.3$ . Calc.,  $\text{C}=62.1$ ;  $\text{H}=10.3$  per cent.)

*The Solid Acids.*—These acids, when distilled under diminished pressure, passed over between  $220^{\circ}$  and  $260^{\circ}/15$  mm. as a light, yellow oil, which solidified on cooling to a crystalline mass, and amounted to 8 grams. The mass was recrystallised from ethyl acetate, when a product was obtained which melted at  $53\text{--}55^{\circ}$ :

0.2528 gave 0.6948  $\text{CO}_2$  and 0.2870  $\text{H}_2\text{O}$ .  $\text{C}=74.9$ ;  $\text{H}=12.6$ .

$\text{C}_{16}\text{H}_{32}\text{O}_2$  requires  $\text{C}=75.0$ ;  $\text{H}=12.5$  per cent.

$\text{C}_{18}\text{H}_{36}\text{O}_2$  „  $\text{C}=76.1$ ;  $\text{H}=12.7$  „ „

The solid product thus appeared to consist of a mixture of palmitic and stearic acids, the former predominating.

### II.—*Ethereal Extract of the Resin.*

This extract, after the removal of the solvent, was a dark resinous mass, which could easily be reduced to a light brown powder, and was stable in the air. It amounted to 725 grams.

After treatment with a little animal charcoal, the optical rotatory power of the resin was determined, with the following result:

A solution in absolute alcohol, of which 5 c.c. contained 0.2072 gram of the resin, gave  $\alpha_D - 0^\circ 51'$  in a 1-dcm. tube, whence  $[\alpha]_D - 20.5^\circ$ .

*Hydrolysis of the Ethereal Extract with Barium Hydroxide.*

A quantity (500 grams) of the dry ethereal extract of the resin was dissolved in alcohol, and, after the addition of a little water, a cold saturated solution of barium hydroxide was gradually added until the liquid showed an alkaline reaction. It was then kept at a temperature of  $35-45^\circ$ , and the alkalinity maintained by the further occasional addition of small portions of solution of barium hydroxide. This treatment was continued until the liquid gave no turbidity when mixed with water, after which it was allowed to cool, and a dark brown precipitate which had formed during the hydrolysis was separated by filtration.

*Isolation of Ipuranol,  $C_{23}H_{38}O_2(OH)_2$ .*

The above-mentioned dark brown precipitate amounted to 50 grams, and consisted for the most part of a barium salt. It was treated with acetic acid, when a portion remained undissolved, and this, after being dried, was extracted in a Soxhlet apparatus with absolute alcohol. A small amount of a sparingly soluble substance was thus removed, which, after several crystallisations from dilute pyridine, was obtained in colourless, microscopic needles, melting at  $285-290^\circ$ . After drying at  $110^\circ$ , it was analysed. (Found,  $C=72.4$ ;  $H=10.6$ . Calc.,  $C=72.6$ ;  $H=10.5$  per cent.)

This substance was evidently ipuranol, the identity of which was further confirmed by the colour reactions and the formation of the acetyl derivative, which separated from ethyl acetate in needles melting at  $162^\circ$ .

The liquid from which the above-mentioned dark brown precipitate had been separated by filtration was diluted with a large volume of water, and distilled in a current of steam in order to remove the alcohol. The excess of barium was then removed by carbon dioxide, and, after boiling and filtering, dilute sulphuric acid was added to the liquid until a precipitate just ceased to be produced, any excess of the mineral acid being carefully avoided. The liquid was again filtered to remove the barium sulphate, and then distilled in a current of steam until volatile acids ceased to pass over.



*Isolation of d- $\alpha$ -Methylbutyric and Tiglic Acids.*

The above-mentioned distillate was a slightly opalescent liquid, amounting to about 8 litres. It was neutralised with sodium carbonate, and concentrated to a small volume, then acidified and extracted with ether, the ethereal liquid being dried and the solvent removed. A quantity (40 grams) of liquid acid was thus obtained, which, when distilled under the ordinary pressure, passed over between 160° and 200°, and it was observed that the last portions of the distillate, on cooling, solidified to a colourless, crystalline mass. Although the greater part of the solid acid, which was unsaturated, could be removed from the liquid portion by repeated fractional distillation, a complete separation could not thus be effected. In order, therefore, to obtain the liquid acid in a pure state, it was finally treated with potassium permanganate in alkaline solution at 0°. On subsequently recovering the unchanged acid, it was found to distil at 172—175°, and to possess the odour of a valeric acid. (Found, C=58·6; H=10·0. Calc., C=58·8; H=9·8 per cent.)

The density of the acid was 0·9392 at 21°, and a determination of its specific rotatory power gave the following result:

$\alpha_D$ , in a 25 mm. tube at 21°, = +4°8', whence  $[\alpha]_D + 17·6^\circ$ .

It was thus evident that the above-described liquid consisted of the optically active valeric acid (*d- $\alpha$ -methylbutyric acid*), which had previously been obtained from several convolvulaceous resins.

The solid acid which separated from the final fractions of the above-mentioned volatile acids was collected, and recrystallised from water, when it separated in flat needles, melting at 64—65°. By the slow evaporation of its ethereal solution it was obtained in large, well-defined prisms. It instantly decolorised an alkaline solution of potassium permanganate at 0°, and was therefore unsaturated. (Found, C=59·9; H=8·2. Calc., C=60·0; H=8·0 per cent.)

This substance was thus identified as tiglic acid.

The aqueous liquid, from which the above-described acids had been extracted with ether, was distilled in a current of steam. The distillate contained formic acid, together with apparently a little valeric acid.

*Non-volatile Products of the Alkaline Hydrolysis.*—After the removal of the *d- $\alpha$ -methylbutyric* and tiglic acids by distillation with steam, as above described, there remained in the distillation flask a dark yellow liquid, which was filtered and concentrated under diminished pressure to the consistency of a viscid syrup.

This product amounted to 327 grams. When further dried it could be reduced to a light brown powder, which, however, became viscid on exposure to the air. It was freely soluble in water, and did not reduce Fehling's solution until after boiling with a dilute mineral acid.

The total amount of the above-mentioned syrupy product was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum, ether, chloroform, ethyl acetate, and alcohol. The light petroleum removed nothing, and, after extracting with the three succeeding solvents, nothing further was removed by the alcohol.

*Ether and Chloroform Extracts of the Hydrolysed Resin (II).*

These extracts were dark-coloured, viscid masses, amounting to 25 and 2 grams respectively. They were sparingly soluble in water, and after heating with a 5 per cent. solution of sulphuric acid in aqueous alcohol, nothing definite could be isolated. The liquids obtained by this treatment reduced Fehling's solution, but no osazone could be prepared from them.

*Ethyl Acetate Extract of the Hydrolysed Resin (II).*

This was a colourless, semi-crystalline mass, amounting to 300 grams. When thoroughly dried, it could be reduced to a fine, white powder, which was not hygroscopic. It was only sparingly soluble in ethyl acetate, even when hot, but readily soluble in alcohol, acetone, and water. The aqueous solution was optically active, and a determination of its specific rotatory power gave the following result:

0.7750, made up to 20 c.c. with distilled water, gave  $\alpha_D - 2^{\circ}55'$  in a 2-dcm. tube, whence  $[\alpha]_D - 37.62^{\circ}$ .

A quantity (200 grams) of the above-described product was heated for about three hours in a reflux apparatus with ten times its weight of aqueous 5 per cent. sulphuric acid, and the liquid then distilled in a current of steam. The distillate, which amounted to 3 litres, was first extracted with ether, when a small amount of an oil was removed, which partly solidified. The oily portion gave the colour reaction for furfuraldehyde, whilst the solid substance, which separated from ethyl acetate in laminæ melting at  $44^{\circ}$ , appeared to consist of methyl jalapinate, a compound which was obtained in somewhat larger amount from the non-volatile products of the acid hydrolysis. The aqueous distillate, after extraction



with ether, was found to contain a little formic acid, with apparently traces of a valeric acid.

After the removal of the volatile products resulting from the above-described acid hydrolysis, there remained in the distillation flask about 3 litres of a dark yellow liquid, together with a quantity of solid material which floated on the surface. The whole was extracted with ether, when all of the solid material passed into solution. On subsequently extracting the ethereal liquid with aqueous sodium carbonate, a quantity of the sodium salt of an organic acid separated, and this was collected. The ethereal liquid was then dried, and the solvent removed, when a small amount (0.5 gram) of a light-coloured oil remained, which became solid on cooling. This substance was recrystallised from ethyl acetate, when it separated in shining laminæ, melting at 45—46°:

0.1250 gave 0.3244  $\text{CO}_2$  and 0.1350  $\text{H}_2\text{O}$ .  $\text{C}=70.8$ ;  $\text{H}=12.0$ .

$\text{C}_{17}\text{H}_{34}\text{O}_3$  requires  $\text{C}=71.3$ ;  $\text{H}=11.9$  per cent.

On heating a portion of the substance with alcoholic potassium hydroxide it was found to become hydrolysed, and an acid was thus obtained, which separated from ethyl acetate in small needles, melting at 67—68°. (Found,  $\text{C}=70.2$ ;  $\text{H}=11.8$ . Calc.,  $\text{C}=70.6$ ;  $\text{H}=11.7$  per cent.)

The above-described substance was thus identified as methyl jalapinolate, which had evidently escaped hydrolysis by the preceding treatment with dilute sulphuric acid.

Small amounts of methyl jalapinolate were subsequently isolated from the various products resulting from the alkaline hydrolysis of the original ethyl acetate extract of the resin. It was therefore deemed of interest to ascertain what proportion of the hydrolysed ethereal extract of the original resin was acidic, as a portion of it evidently consisted of a derivative of methyl jalapinolate. For this purpose a quantity (10 grams) of the hydrolysed resin was acetylated by means of acetic anhydride, the product dissolved in ether, and the ethereal liquid shaken with aqueous potassium hydroxide. By this means 6.7 grams of acidic material were removed, which formed a yellow, amorphous, friable mass, and on subsequently evaporating the ether, 6.4 grams of a neutral, light yellow syrup were obtained. After hydrolysis with barium hydroxide the product from the acidic portion had  $[\alpha]_D -35.7^\circ$ , whilst that from the neutral portion had  $[\alpha]_D -35.1^\circ$ . Both these products, on heating with dilute sulphuric acid, yielded jalapinic acid and a mixture of sugars, the neutral acetyl derivative also giving a trace of methyl jalapinolate.

*Isolation of Jalapinolic Acid,  $C_{15}H_{30}(OH) \cdot CO_2H$ .  
(Hydroxyhexadecylic Acid.)*

The sodium salt, obtained by extracting the ethereal liquid with sodium carbonate, as above described, was decomposed with dilute sulphuric acid, and the liberated organic acid taken up with ether. On removing the solvent, a quantity (62 grams) of an oily product was obtained, which solidified on cooling to a crystalline mass. This was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively with (a) light petroleum, and (b) ether.

(a) *Petroleum Extract*.—This was a white, fatty mass, amounting to 48 grams. It was converted into the methyl ester by dissolving in methyl alcohol and saturating the solution with dry hydrogen chloride. On subsequently pouring the acid liquid into water, and extracting with ether, a product was obtained, which, when distilled under diminished pressure, passed over at  $220^{\circ}/20$  mm. as a colourless oil, and, on cooling, solidified to a white, crystalline mass. On recrystallising the distilled ester from ethyl acetate, it separated in handsome laminae, melting at  $47-49^{\circ}$ . (Found,  $C=71.0$ ;  $H=11.9$ . Calc.,  $C=71.3$ ;  $H=11.9$  per cent.)

The optical rotatory power of the ester was determined, with the following result:

2.8756, made up to 20 c.c. with chloroform, gave  $\alpha_D + 0^{\circ}17'$  in a 2-dcm. tube, whence  $[\alpha]_D + 0.98^{\circ}$ .

The ester was then hydrolysed by boiling with an alcoholic solution of potassium hydroxide, the alcohol removed, and the liquid acidified, when an acid was obtained, which separated from dilute acetic acid in fine, silky needles, melting at  $67-68^{\circ}$ . (Found,  $C=70.7$ ;  $H=11.8$ . Neutralisation value = 209.3. Calc.,  $C=70.6$ ;  $H=11.7$  per cent. Neutralisation value = 206.2.)

The above-described acid is thus seen to be jalapinolic acid, a compound which was first obtained by Mayer from "jalapin" (*Annalen*, 1855, **95**, 149), and subsequently investigated by Kromer (*J. pr. Chem.*, 1898, [ii], **57**, 448). The last-mentioned investigator stated that jalapinolic acid is optically inactive, which is not correct, although its rotatory power is comparatively small\*:

\* Having observed the optical activity of jalapinolic acid, it seemed desirable to examine in this respect two other hydroxy-acids which had previously been obtained from convolvulaceous resins, namely: convolvulinolic acid (*J. Amer. Chem. Soc.*, 1910, **32**, 106) and ipurolic acid, (*ibid.*, p. 107, and *Amer. J. Pharm.*, 1908, **80**, 273).

Convolvulinolic acid,  $C_{14}H_{28}(OH) \cdot CO_2H$  (m. p.  $51-52^{\circ}$ ): 4.1738, made up to 20 c.c. with chloroform, gave  $\alpha_D + 0^{\circ}35'$  in a 2-dcm. tube, whence  $[\alpha]_D + 1.39^{\circ}$ .



3.5518, made up to 20 c.c. with chloroform, gave  $\alpha_D + 0^\circ 17'$  in a 2-dcm. tube, whence  $[\alpha]_D + 0.79^\circ$ .

(b) *Ethereal Extract*.—The acid extracted by ether was dark in colour, and amounted to 12 grams. It was purified by conversion into its methyl ester, and found to consist only of jalapinic acid.

*Identification of Dextrose and a Methylpentose.*

The aqueous acid liquid resulting from the acid hydrolysis of the ethyl acetate extract of the hydrolysed resin, which had been extracted with ether as above described, was subsequently treated with barium hydroxide for the removal of the sulphuric acid, the mixture filtered, and the filtrate evaporated under diminished pressure to the consistency of a syrup. This syrup readily reduced Fehling's solution, and yielded an osazone, melting at  $203\text{--}205^\circ$ , which was evidently *d*-phenylglucosazone.

In order to obtain more definite information respecting the character of the sugar produced by the above-mentioned hydrolysis, the syrup was heated with acetic anhydride in the presence of a trace of *d*-camphorsulphonic acid. A vigorous reaction ensued, and after this had subsided the mixture was cooled, poured into water, and the liquid extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when a quantity of a light-coloured syrup remained, which was dissolved in dilute alcohol. After keeping for a few days a crystalline substance separated, which was collected and recrystallised from 70 per cent. alcohol, when it was deposited in handsome, prismatic needles, melting at  $142\text{--}143^\circ$ . It was anhydrous, and gave on analysis the following results:

0.2466 gave 0.4582  $\text{CO}_2$  and 0.1358  $\text{H}_2\text{O}$ .  $\text{C} = 50.6$ ;  $\text{H} = 6.1$ .

0.1070 „ 0.1986  $\text{CO}_2$  „ 0.0606  $\text{H}_2\text{O}$ .  $\text{C} = 50.6$ ;  $\text{H} = 6.3$ .

$\text{C}_{14}\text{H}_{20}\text{O}_9$  requires  $\text{C} = 50.6$ ;  $\text{H} = 6.0$  per cent.

The above-described substance is thus seen to be a *tetra-acetyl-methylpentose*,  $\text{C}_6\text{H}_8\text{O}_5(\text{CO}\cdot\text{CH}_3)_4$ , and it is apparently a new compound. A determination of its optical rotatory power gave the following result:

Methyl convolvulinolate,  $\text{C}_{14}\text{H}_{28}(\text{OH})\cdot\text{CO}_2\cdot\text{CH}_3$  (m. p.  $32\text{--}33^\circ$ ): 2.0142, made up to 20 c.c. with chloroform, gave  $\alpha_D + 0^\circ 19'$  in a 2-dcm. tube, whence  $[\alpha]_D + 1.57^\circ$ .

Ipurollic acid,  $\text{C}_{13}\text{H}_{25}(\text{OH})_2\cdot\text{CO}_2\text{H}$  (m. p.  $100\text{--}101^\circ$ ).

No rotation could be measured with a solution of 2.6068 of the acid in 20 c.c. of absolute alcohol.

Methyl ipurolate,  $\text{C}_{13}\text{H}_{25}(\text{OH})_2\cdot\text{CO}_2\cdot\text{CH}_3$  (m.p.  $68\text{--}69^\circ$ ): 0.6900, made up to 20 c.c. with absolute alcohol, gave  $\alpha_D + 0^\circ 7'$  in a 2-dcm. tube, whence  $[\alpha]_D + 1.69^\circ$ .

0.7238, made up to 20 c.c. with chloroform, gave  $\alpha_D + 1^\circ 34'$  in a 2-dcm. tube, whence  $[\alpha]_D + 21.64^\circ$ .

The sugar obtained by hydrolysing a small portion of the above-described acetyl derivative yielded an osazone melting at  $180\text{--}182^\circ$ , but this was not identical with rhamnosazone, for a mixture of the two compounds melted at  $163\text{--}164^\circ$ . Moreover, on acetylating a quantity of pure rhamnose no crystalline derivative could be obtained.

For the purpose of comparing the properties of the sugar yielding the above-described tetra-acetyl derivative with those of rhodose, a small quantity of the latter was kindly supplied to us by Professor E. Votoček, of Prague. This substance was in colourless, prismatic needles, melting at  $144\text{--}145^\circ$ , but the acetylated product could only be obtained in the form of a syrup. It may, furthermore, be noted that the phenylosazone of rhodose has been recorded as melting at  $170^\circ$  (*Chem. Centr.*, 1900, I., p. 803). *isoRhodose* yields an osazone melting at  $186\text{--}187^\circ$ , but the benzoylated product could not be obtained in a crystalline state (Votoček, *Ber.*, 1911, **44**, 820). In order to ascertain whether the methylpentose contained in the above-mentioned syrup was capable of yielding a crystalline benzoyl derivative, portions of the syrup were treated by both the Schotten-Baumann method and by heating with benzoic anhydride, but in each case with a negative result.

After the separation of the above-described tetra-acetylmethylpentose, the mother liquors yielded a further quantity of the same substance, and finally a more readily soluble solid was deposited. This was collected, washed with a little dilute alcohol, and then recrystallised from 70 per cent. alcohol, when it separated in slender needles, melting at  $111\text{--}112^\circ$ . After two further crystallisations the substance began to melt at  $112^\circ$ , but complete fusion only took place at  $118^\circ$ . (Found, C=49.2; H=5.7. Calc., C=49.2; H=5.6 per cent.)

This compound was thus identified as penta-acetyldextrose,  $\text{C}_6\text{H}_7\text{O}_6(\text{CO}\cdot\text{CH}_3)_5$ , and it apparently consisted of a mixture of the  $\alpha$ - and  $\beta$ -forms, which melt at  $112^\circ$  and  $134^\circ$  respectively.

From the above results it is evident that by the acid hydrolysis of the ethyl acetate-soluble portion of the hydrolysed ethereal extract of the resin, two sugars are produced, one of which is dextrose, and in predominating amount, whilst the other is a methylpentose.



*Oxidation of the Ethyl Acetate Extract of the Hydrolysed Resin with Nitric Acid.*

A quantity (25 grams) of the previously-described ethyl acetate extract of the hydrolysed resin was dissolved in a little water, and to the solution, contained in a flask provided with a reflux condenser, 200 grams of nitric acid (D 1·4) were added. The mixture was then gently warmed, when a vigorous reaction ensued, and after this had ceased the heating was continued for a short time. About 200 c.c. of water were subsequently added, the mixture boiled for ten minutes, and then distilled in a current of steam. The distillate was rendered alkaline with sodium carbonate, concentrated to a small bulk, then acidified with hydrochloric acid, and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A small amount (1·2 grams) of a liquid acid was thus obtained, which, when distilled under the ordinary pressure, passed over between 190° and 195° as a colourless oil, and was dextro-rotatory:

0·1578 gave 0·3494 CO<sub>2</sub> and 0·1434 H<sub>2</sub>O. C=60·3; H=10·1.

C<sub>5</sub>H<sub>10</sub>O<sub>2</sub> requires C=58·8; H=9·8 per cent.

C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> „ C=62·0; H=10·3 „ „

A portion of the acid was converted into a silver salt, which was precipitated in three fractions, and these were analysed:

(a) 0·3020 gave 0·1456 Ag. Ag=48·2.

(b) 0·2962 „ 0·1440 Ag. Ag=48·6.

(c) 0·2320 „ 0·1180 Ag. Ag=50·9.

C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>Ag requires Ag=51·7 per cent.

C<sub>6</sub>H<sub>11</sub>O<sub>2</sub>Ag „ Ag=48·4 „ „

It would thus appear that the volatile acid formed by the oxidation consisted of a mixture of optically active valeric acid and a hexoic acid.

The aqueous acid liquid remaining in the distillation flask deposited a white solid on cooling. The mixture was accordingly extracted with ether, and the ethereal liquid shaken with aqueous sodium carbonate, which removed all of the dissolved substance. On subsequently acidifying the alkaline liquid and extracting with ether, it yielded a quantity (3 grams) of a solid acid, which was fractionally crystallised, first from dilute acetic acid, and finally from the glacial acid. Four fractions were thus obtained, which melted at 125—127°, 115—117°, 104—107°, and 84—90° respectively. After drying in a vacuum and then at 120°, they were analysed:

- I. 0.0956 gave 0.2092 CO<sub>2</sub> and 0.0792 H<sub>2</sub>O. C=59.6; H=9.2.  
 II. 0.1084 „ 0.2358 CO<sub>2</sub> „ 0.0884 H<sub>2</sub>O. C=59.3; H=9.0.  
 III. 0.1434 „ 0.3176 CO<sub>2</sub> „ 0.1190 H<sub>2</sub>O. C=60.4; H=9.2.  
 IV. 0.1704 „ 0.3730 CO<sub>2</sub> „ 0.1394 H<sub>2</sub>O. C=59.7; H=9.1.  
 C<sub>10</sub>H<sub>18</sub>O<sub>4</sub> requires C=59.4; H=8.9 per cent.  
 C<sub>11</sub>H<sub>20</sub>O<sub>4</sub> „ C=61.1; H=9.3 „ „

These results would thus indicate that the non-volatile acids produced by the oxidation of the above-described glucosidic substance consist of a mixture of sebacic and *n*-nonanedicarboxylic acids. The first mother liquors from the crystallisation of these acids also contained a small amount of oxalic acid, which was evidently produced from the sugar complex of the glucoside.

Kromer (*J. pr. Chem.*, 1898, [ii], 57, 448), in investigating the jalapinolic acid obtained from the so-called "false jalap," observed it to yield, on oxidation with alkaline potassium permanganate,  $\alpha$ -methylbutyric and sebacic acids, together with an acid melting at 89—91°, which was thought to be isomeric with the latter. From these results he concluded that the constitution of jalapinolic acid could be represented as follows: CHMeEt·CH(OH)·[CH<sub>2</sub>]<sub>10</sub>·CO<sub>2</sub>H.

As already noted, it has now been ascertained that jalapinolic acid is optically active, but inasmuch as the oxidation products of the above-described glucosidic substance appear to consist most largely of sebacic acid and a hexoic acid, it is more probable that the respective acid possesses the following formula:



### III.—*Chloroform Extract of the Resin.*

This was a dark, resinous product, amounting to only 8 grams. It was heated with dilute sulphuric acid in aqueous alcohol, but no crystalline substance could be isolated after this treatment, and although the resulting aqueous liquid reduced Fehling's solution, no osazone could be prepared from it.

### IV.—*Ethyl Acetate Extract of the Resin.*

This extract, after the removal of the solvent, formed a dark-coloured mass, and amounted to 295 grams. When dissolved in alcohol, and treated with animal charcoal, a product was obtained which could be reduced to a nearly white powder. Its optical rotatory power was determined, with the following result:

A solution in absolute alcohol, of which 5 c.c. contained 0.5086 gram of substance, gave  $\alpha_D - 2^\circ 51'$  in a 1-dcm. tube, whence  $[\alpha]_D - 28.01^\circ$ .



*Hydrolysis of the Ethyl Acetate Extract with Barium Hydroxide.*

A quantity (250 grams) of the ethyl acetate extract of the resin was dissolved in alcohol, a little water added, and subsequently a slight excess of a cold saturated solution of barium hydroxide. The hydrolysis was then allowed to proceed in precisely the same manner as described in connexion with the ether extract of the resin. After the hydrolysis was complete the filtered liquid was diluted with a large volume of water, and the alcohol removed by distillation in a current of steam. The barium contained in the solution was then exactly precipitated with dilute sulphuric acid, and the filtered liquid again distilled in steam until acid ceased to pass over. The distillate was rendered alkaline with sodium carbonate, concentrated to a small volume, then acidified, and extracted with ether. The aqueous liquid remaining after this treatment was found to contain a considerable amount of acetic acid, but no formic acid. On subsequently evaporating the ethereal liquid, a quantity (15 grams) of a colourless liquid acid was obtained, which was distilled under the ordinary pressure, and the following fractions collected: (1) 100—125°; (2) 125—150°; (3) 150—170°; (4) 170—180°; (5) 180—185°; (6) 185—195°. The last fraction, amounting to 0·5 gram, almost completely solidified.

It was evident from the above results that the volatile acids consisted of a rather complex mixture. Fractions 1, 2, and 3 were each converted into three fractions of silver salt, the analysis of which indicated the presence of a considerable proportion of acetic acid with apparently some valeric acid. Fractions 4, 5, and the liquid portion of 6 were united, and treated in alkaline solution with potassium permanganate, as described in connexion with the volatile acids obtained by the hydrolysis of the ethereal extract of the resin with barium hydroxide. The amount of acid recovered after this treatment was 4·1 grams. It distilled between 173° and 175°, and possessed the following constants:  $D_{21}^{21}$  0·9320;  $\alpha_D + 4\cdot 07'$  in a 25 mm. tube, whence  $[\alpha]_D + 17\cdot 6^\circ$ . (Found, C=57·6; H=9·7. Calc., C=58·8; H=9·8 per cent.)

The above-described acid thus appears to have consisted chiefly of the optically active valeric acid, with a little acetic acid.

The solid acid contained in fraction 6 was recrystallised from water, when it separated in needles melting at 64—65°, and was identified as tiglic acid. (Found, C=60·0; H=8·2. Calc., C=60·0; H=8·0 per cent.)

The aqueous liquid remaining in the distillation flask after the removal of the above-mentioned volatile acids was filtered, and concentrated under diminished pressure to a syrup. The latter

was then dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture successively extracted in a Soxhlet apparatus with ether, chloroform, ethyl acetate, and alcohol.

*Ether and Chloroform Extracts of the Hydrolysed Resin (IV).*

These extracts were dark-coloured syrups, amounting to 12.5 and 2.3 grams respectively. They were only sparingly soluble in water, and were therefore heated with 5 per cent. sulphuric acid in aqueous alcohol. In both cases a very small amount of methyl jalapinate was isolated from the neutral non-volatile portion of the product, and from the ethereal extract a small amount of jalapinic acid was also obtained.

*Ethyl Acetate Extract of the Hydrolysed Resin (IV).*

This was an amorphous solid, which could easily be reduced to a light-coloured powder, and was not hygroscopic. It was readily soluble in cold water, yielding a clear liquid, which did not reduce Fehling's solution until after heating with an acid. It was optically active, and a determination of its specific rotatory power gave the following result:

A solution, of which 5 c.c. gave on evaporation 0.1650 gram of substance, dried at  $110^{\circ}$ , had  $\alpha_D -2^{\circ}9'$  in a 2-dcm. tube, whence  $[\alpha]_D -32.62^{\circ}$ .

*Treatment with Dilute Sulphuric Acid.*—A solution containing 25 grams of the above-described product in 500 grams of 5 per cent. aqueous sulphuric acid, was heated for about four hours in a reflux apparatus, and the liquid then distilled in a current of steam. The volatile product appeared to consist only of traces of furfuraldehyde and formic acid.

After the above operation there remained in the distillation flask a dark yellow liquid with a cake of solid substance floating on the surface. The whole was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. On subsequently evaporating the ether, a small amount of a neutral substance was obtained, which, when recrystallised from ethyl acetate, separated in leaflets melting at  $45-46^{\circ}$ , and was identified as methyl jalapinate. The sodium carbonate extract was then acidified and extracted with ether, when a quantity of a dark-coloured product was obtained. This was dissolved in alcohol, mixed with purified sawdust, and the dried mixture extracted successively with light petroleum and ether. The petroleum removed a quantity (3 grams) of a white solid, which, when crystallised from dilute acetic acid, separated in needles melting at  $67-68^{\circ}$ , and proved to be jalapinic



acid,  $C_{16}H_{32}O_3$ . (Found,  $C=70.5$ ;  $H=11.8$ . Calc.,  $C=70.6$ ;  $H=11.7$  per cent.) A large amount of this acid had previously been obtained from the ethereal extract of the original resin after alkaline hydrolysis and extraction with ethyl acetate.

By the subsequent extraction of the above-mentioned mixture with ether, a further quantity (about 2 grams) of an acidic product was obtained, which was dark in colour. It was therefore purified by conversion into its methyl ester, which distilled at  $220/20$  mm., and, after crystallisation from ethyl acetate, melted at  $47-49^\circ$ . The portion of acidic product removed by ether was thus shown to consist of impure jalapinic acid.

The above-described yellow aqueous liquid, which had been extracted with ether, was finally treated with barium hydroxide for the removal of the sulphuric acid, and, after filtration, was concentrated under diminished pressure. It then yielded an osazone, which separated from dilute pyridine in clusters of fine needles, melting at  $180-182^\circ$ , and was doubtless a derivative of the previously described methylpentose. No dextrose was present in the liquid.

#### *Alcohol Extract of the Hydrolysed Resin (IV).*

This was an amorphous solid, which amounted to 100 grams, and, after treatment with animal charcoal, was obtained as a perfectly white powder. It was readily soluble in water, and did not reduce Fehling's solution until after heating with an acid. It was optically active, and a determination of its specific rotatory power gave the following result:

A solution, of which 5 c.c. gave on evaporation 0.3200 gram of substance, dried at  $110^\circ$ , had  $\alpha_D -4.26'$  in a 2-dcm. tube, whence  $[\alpha]_D -34.64^\circ$ .

*Treatment with Dilute Sulphuric Acid.*—Seventy grams of the above-described product were dissolved in water, and such an amount of dilute sulphuric acid added as to form 1200 grams of solution containing 5 per cent. of acid. The whole was then heated in a reflux apparatus for about four hours, after which it was distilled in a current of steam. The only volatile products obtained by this treatment were a little oil giving the colour reaction of furfuraldehyde and a small amount of formic acid.

After the above operation there remained in the distillation flask a dark yellow liquid and a quantity of solid substance floating on the surface. The whole was extracted with ether, and the ethereal liquid shaken with aqueous sodium carbonate. On evaporating the ether, a small amount of substance was obtained, which, when crystallised from ethyl acetate, separated in leaflets melting at

45—46°, and was evidently methyl jalapinate. The sodium carbonate extract, when acidified and extracted with ether, yielded a quantity of acid, which was dissolved in alcohol, mixed with purified sawdust, and extracted successively with light petroleum and ether, as described in connexion with the corresponding product from the ethyl acetate extract of the hydrolysed resin (IV). The petroleum extract amounted to 2·5 grams, and after crystallisation from dilute acetic acid was obtained in colourless needles, melting at 67—68°. This substance consisted of pure jalapinic acid,  $C_{16}H_{32}O_8$ . (Found, C=70·6; H=11·8. Calc., C=70·6; H=11·7 per cent.) The acid contained in the ethereal extract, being dark in colour, was converted into its methyl ester, and the product distilled under diminished pressure, when it passed over at 220°/20 mm. as a nearly colourless oil, which solidified on cooling to a crystalline mass. It was recrystallised from ethyl acetate, when it separated in beautiful, colourless laminae, melting at 47—49°. The amount of this ester was 13 grams, and it consisted of methyl jalapinate.

The yellow aqueous liquid which had been extracted with ether as above described, was treated with barium hydroxide for the removal of the sulphuric acid, and, after filtration, concentrated under diminished pressure. The resulting syrup when treated by the method described by A. G. Perkin (Trans., 1910, **97**, 1777) yielded two osazones, one of which, and the larger in amount, melted at 203—205°, and was doubtless *d*-phenylglucosazone, whilst the other, after crystallisation from dilute pyridine, melted at 180—182°. The compound melting at 180—182° was not rhamnosazone, but evidently derived from another methylpentose, inasmuch as a portion of the above-mentioned syrup, when treated with acetic anhydride, yielded the same crystalline tetra-acetyl derivative (m. p. 142°) as has already been described in connexion with the portion of the hydrolysed ethereal extract of the resin (II) which was soluble in ethyl acetate. Penta-acetyldextrose (m. p. 112°) was also obtained by this treatment.

#### V.—*Alcohol Extract of the Resin.*

This was a black, amorphous solid, amounting to 20 grams. When heated with dilute sulphuric acid in aqueous alcohol, it yielded traces of formic acid and a sugar from which *d*-phenylglucosazone (m. p. 204—205°) was prepared. It was therefore glucosidic in character.



*Summary.*

The material employed for this investigation consisted of the roots of *Ipomoea orizabensis*, Ledanois (Nat. Ord. *Convolvulaceae*), which are commonly known as "Mexican Scammony Root."

The root was found to contain 14.55 per cent. of resin, 71 per cent. of which was soluble in ether. After treatment with animal charcoal the resin was obtained nearly colourless. It then melted at 125—130°, and had  $[\alpha]_D - 23.0^\circ$ .

For a complete examination of the root, 48.76 kilograms of the ground material were extracted with hot alcohol. A portion of the concentrated extract was employed for determining the presence of sucrose, and a small amount of the latter was isolated. Another portion of the extract was distilled in a current of steam, when a very small amount of a pale yellow essential oil was obtained. From the portion of the extract which was soluble in water, the following compounds were isolated: (i) scopoletin,  $C_{10}H_8O_4$  (m. p. 203—204°), a small proportion of which appeared to be present in the form of a glucoside; (ii) 3:4-dihydroxycinnamic acid,  $C_9H_8O_4$  (m. p. 223—225°), from which the *methyl* ester (m. p. 158—160°) was prepared. The aqueous liquid contained, furthermore, a quantity of sugar, which yielded *d*-phenylglucosazone (m. p. 205—206°).

The portion of the alcoholic extract which was insoluble in water consisted of a resin which possessed the above-mentioned characters. The resin was first successively extracted with various solvents, and the resulting extracts were then further examined.

I. *Petroleum Extract of the Resin.*—From this extract the following substances were obtained: (i) hentriacontane,  $C_{31}H_{64}$ ; (ii) a phytosterol,  $C_{27}H_{46}O$ ; (iii) cetyl alcohol,  $C_{16}H_{34}O$ ; (iv) a mixture of fatty acids, consisting of palmitic, stearic, oleic, and linolenic acids.

II. *Ethereal Extract of the Resin.*—The optical rotatory power of this extract was  $[\alpha]_D - 20.5^\circ$ . After hydrolysis with barium hydroxide it yielded: (i) ipuranol,  $C_{23}H_{38}O_2(OH)_2$ ; (ii) *d*- $\alpha$ -methylbutyric acid; (iii) tiglic acid; and a product which on acid hydrolysis gave (iv) jalapinolic acid,  $C_{15}H_{30}(OH) \cdot CO_2H$  (m. p. 67—68°;  $[\alpha]_D + 0.79^\circ$ ), together with a little methyl jalapinolate, and (v) a mixture of sugars, consisting of dextrose and a methylpentose. The latter yielded an osazone melting at 180—182°, and a *tetra-acetyl* derivative,  $C_6H_8O_5(CO \cdot CH_3)_4$ , which apparently is a new compound. This derivative crystallises in handsome, prismatic needles, melting at 142—143°, and has  $[\alpha]_D + 21.64^\circ$ . The ethyl acetate extract of the product resulting from the alkaline hydrolysis of the ethereal extract of the resin gave on oxidation with nitric acid a mixture

of acids, consisting apparently of optically active valeric and hexoic acids, together with sebacic and *n*-nonanedicarboxylic acids.

III. *Chloroform Extract of the Resin*.—This was relatively small in amount, and consisted of a dark resinous product.

IV. *Ethyl Acetate Extract of the Resin*.—The optical rotatory power of this extract was  $[\alpha]_D -28.01^\circ$ . After hydrolysis with barium hydroxide it yielded products from which the same substances were obtained as from the ethereal extract of the resin, with the exception of the small amount of ipuranol.

V. *Alcohol Extract of the Resin*.—This was a black, amorphous product of a glucosidic nature, but which yielded nothing definite on hydrolysis.

From the results of the present investigation it will be apparent that the resin of *Ipomoea orizabensis* is an exceedingly complex mixture, the constituents of which are, for the most part, amorphous, and not entirely glucosidic. It follows, therefore, that the so-called "jalapin," which includes all the constituents of the resin that are soluble in ether, cannot be represented by any of the various formulæ hitherto assigned to it. It may also be noted that the portion of this resin which is soluble in ether is not identical with the ether-soluble portion of jalap resin, as has previously been affirmed.

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